DEVELOPMENT AND UTILIZATION OF AEROBIC GRANULAR BIOMASS IN PALM OIL MILL EFFLUENT (POME) TREATMENT

by

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Thesis submitted in fulfillment of the requirements for the degree of Master of Science

JULY 2011

ACKNOWLEDGEMENT

I would like to express my deepest gratitude towards The Great Almighty Ganesha, who grants me the knowledge, strength and determination to accomplish Masters research work. My parents, Madam Vijaya Kothandaraman and Mr. Kanadasan Pachiappan who bestowed me with love needs special mention for me able to complete this research work. Their prayers, encouragement, patience and most importantly understanding the process of completing Masters has motivated and driven me throughout my studies.

Dr.Vel Murugan Vadivelu as my main supervisor has guided, motivated and inspired me throughout this period. His stupendous ideas and vision have been the reason for this research to be successfully completed in time and with encouraging results. I would like express my humble gratitude towards my co-supervisor, Assoc. Prof. Dr.Mashitah Mat Don, who gave me invaluable tips and helped me to rectify my mistakes while doing this research.

My appreciation also goes to Dean, Prof. Dr. Azlina bt. Harun @ Kamaruddin and Deputy Dean, Assoc. Prof. Dr. Lee Keat Teong for their continuous support and help rendered throughout my studies.

I am very much indebted to USM Fellowship program for providing financial assistance in the form of scholarship. Besides that, the grant provided by Universiti Sains Malaysia (1001/PJKIMIA/8033025) has helped me while doing this research. To all the technicians, especially Mr. Shamsul Hidayat Shaharan, Mr. Muhd Arif Mat Husin, Madam Yusnadia and Mr. Mohd Roqib Mohd Rashidi who assisted me greatly while doing this research needs a special mention. The undergraduate students, Lunish Sadsivam and Lim Jing Xiang who worked in this project also gratefully acknowledged. Besides that, my colleagues, G.Sivarajah Ganesan, Peyong Yet Nee and Nor Azyati who helped while conducting this research are gratefully acknowledged.

Last but not least, my heart-felt gratitude to my friends and relatives for their endless love and support.

Gobi Kanadasan

April 2011

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A	Weight of sample and filter paper	(mg)
B	Weight of empty filter paper	(mg)
β	Regression coefficient	
C_e	Equilibrium concentration of MB	(mg/l)
C_o	Initial concentration of MB	(mg/l)
C_t	Concentration of MB at time t	(mg/l)
DF	Degree of freedom	
ε %	Standard deviation	
$\Delta G°$	Change in Gibbs Free Energy	(kJ/mol)
$\Delta H°$	Enthalpy change of MB adsorption	(kJ/mol)
i	Linear coefficients	
j	Quadratic coefficients	
K_c	Langmuir constant	
K_F	Freundlich constants	
k_1	Pseudo-first-order rate constant for the adsorption.	(min^{-1})
k_2	pseudo-second-order rate constant	(g/mg.min)
k_{AB}	Adam-Bohart's kinetic constant	(ml/mg.min)
k_{YN}	Yoon-Nelson rate velocity constant	(1/min)
k_{Th}	Thomas rate constant	(ml/min.mg)
L	Linear velocity	(cm/min)
M	Adsorbent mass	(g)
m_{ad}	Total quantity of dye mass adsorbed in the column	(mg)
m_{total}	Total amount of MB sent through the column	(mg)

N_o	Saturation concentration	(mg/ml)
n	Favorability it is towards the adsorption process	
Q_o	Langmuir constants related to adsorption capacity	
Q	Flow rate of MB	(ml/min)
q_e	Amount of MB adsorbed at equilibrium	(mg/g)
q_t	Amount of adsorption at time t	(mg/g)
R	Universal gas constant	(8.314 $Jmol^{-1}K^{-1}$)
R^2	Linear regression coefficients	
$\Delta S°$	Entropy change of MB adsorption	(J/mol.K)
t_b	Bed breakthrough time	(minutes)
t_e	Bed exhaustion time	(minutes)
t	Time	(minutes)
τ_{cal}	Calculated time required for 50% adsorbate breakthrough.	(minutes)
τ_{exp}	Experimental time required for 50% adsorbate breakthrough.	(minutes)
T	Absolute temperature	(K)
v/v%	Volume to volume percentage	%
V	Volume of the solution	(l)
W	Mass of WAS.	(g)
Z	Bed depth of the column	(cm)

LIST OF ABBREVIATION

ANOVA	Analysis of variance
BOD	Biochemical Oxygen Demand
BWT	Biological wastewater treatment
CCD	Central Composite Design
COD	Chemical Oxygen Demand
DO	Dissolved oxygen
DOE	Department of Environment
EFB	Empty fruit brunches
EPS	Extracellular polymeric substances
FFB	Fresh fruit bunch
FTIR	Fourier Transmission Infrared Spectroscopy
H/D	Height over diameter
HRT	Hydraulic retention time
MB	Methylene Blue
MLSS	Mixed liquor suspended solids
OLR	Organic loading rate
POME	Palm oil mill effluent
RSM	Response Surface Methodology
SBR	Sequencing batch reactor
SMZ	Surfactant modified zeolite
SVI	Sludge volume index
UAF	Upflow anaerobic filtration
UASB	Upflow anaerobic sludge blanket reactor
UASFF	Upflow anaerobic sludge fixed film

UFF	Upflow Fixed Film
VOC	Volatile organic component
WAS	Waste activated sludge

PENGHASILAN DAN PENGGUNAAN BIOJISIM BUTIRAN AEROBIK DALAM RAWATAN KUMBAHAN KILANG KELAPA SAWIT

ABSTRAK

Kumbahan kilang kelapa sawit (POME) yang dibuang tanpa rawatan yang wajar mungkin akan menyebabkan masalah pencemaran di Malaysia. Kaedah rawatan biologi lazim yang menggunakan enapcemar teraktif dalam kolam bersiri dianggap usang. Oleh sebab itu, biojisim butiran aerobik dihasilkan dan digunakan untuk rawatan POME dalam reaktor berkelompok penjujukan (SBR). Purata garis pusat butiran aerobik yang dihasilkan adalah 0.9 mm. Butiran aerobik yang dihasilkan telah berjaya menyingkirkan 88% daripada influen COD secara purata sepanjang operasi reaktor ini. Indeks isipadu enapcemar (SVI) biojisim berkurangan dari 80 ke 30 ml/g. Manakala, campuran pencairan pepejal terampai (MLSS) SBR telah berkurangan daripada 3600 ke 2500 mg/l sebelum proses pembutiran dan MLSS telah meningkat ke 3800 mg/l selepas berbutir aerobik terbentuk. Dalam rawatan fizik, kajian permulaan telah dijalankan dengan menggunakan sisa enapcemar teraktif (WAS) dari SBR untuk menjerap Metelina Biru (MB) secara berkelompok dan dalam turus aliran berterusan. Hasil ujikaji menunjukkan penjerapan MB meningkat dengan peningkatan kepekatan awal MB dan pH, manakala penjerapan menurun apabila suhu meningkat. WAS mempunyai keupayaan penjerapan sebanyak 66.23 mg/g, penyingkiran MB 84%, mematuhi garis sesuhu Langmuir dan Freundlich, dan berpadanan dengan pseudo-tertib kedua. Analisa termodinamik menunjukkan bahawa proses penjerapan MB ke atas WAS adalah proses luah haba dan spontan. Manakala dalam turus aliran berterusan, penjerapan meningkat pada kadar aliran yang perlahan, ketinggian yang besar dan kepekatan pencelup yang tinggi. Keupayaan penjerapan dan kecekapan penyingkiran masing-masing adalah

20.16 mg/g dan 82.3%. Data ujikaji berpadanan dengan model Thomas dan model Yoon-Nelson. Dalam bahagian terakhir dalam kajian ini, efluen SBR (POME yang telah dirawat secara biologi) telah dirawat lagi dengan WAS yang dimuatkan dalam turus aliran berterusan. Penyingkiran tertinggi yang dicapai untuk COD dan kekeruhan masing-masing adalah 20.68% dan 99.21%. Nilai optima penyingkiran COD dan kekeruhan (20.68% dan 96.42%, masing-masing) dicapai pada ketinggian turus 3.28 cm dan pada kadar aliran 2.13 ml/min. Hasil menunjukkan bahawa butiran aerobik yang dihasilkan mampu merawat POME secara biologi dan WAS dapat digunakan sebagai penjerap dalam rawatan fizik dengan kecekapan terpuji.

DEVELOPMENT AND UTILIZATION OF AEROBIC GRANULAR BIOMASS IN PALM OIL MILL EFFLUENT (POME) TREATMENT

ABSTRACT

Palm oil mill effluent (POME) discharged without proper treatment could cause severe environmental problem in Malaysia. The conventional biological treatment method using activated sludge in series of ponds is considered obsolete. Hence, in this work, aerobic granular biomass was developed and utilized for the treatment of POME in the sequencing batch reactor (SBR). The mean diameter of the developed aerobic granule was 0.9 mm. The developed aerobic granule managed to remove about 88% of the influent COD at average, throughout the operation of SBR. The sludge volume index (SVI) of the biomass reduced from 80 to 30 ml/g. Meanwhile, the mixed liquor suspended solids (MLSS) of the SBR decreased from 3600 mg/l to 2500 mg/l prior to the granulation process and the MLSS concentration increased to 3800 mg/l after the aerobic granule formed. In the physical treatment, preliminary studies were done by using waste activated sludge (WAS) from SBR to adsorb Methylene Blue (MB) in batch and continuous flow column. Results showed that the uptake of MB increased with an increase in both the initial MB concentration and pH, and decreased with an increase in temperature. WAS was found to have adsorption capacity of 66.23 mg/g, 84% MB removal, obeys both Langmuir and Freundlich isotherm and fits pseudo-second-order kinetics. Thermodynamic analysis showed that the MB adsorption process onto WAS is an exothermic and spontaneous process. Meanwhile in the continuous flow column adsorption, slower flow rate, larger bed height and higher inlet dye concentration increases the adsorption. The adsorption capacity and removal efficiency was 20.16 mg/g and 82.3%, respectively. Data fitted well to Thomas model and Yoon-Nelson model. In the last part of this

study, the effluent from the SBR (biologically treated POME) was further polished using continuous flow column packed with WAS. The optimum value for the COD and turbidity removal (20.68% and 96.42%, respectively) achieved at bed height of 3.28 cm and flow rate of 2.13 ml/min. The results showed that the developed aerobic granule can biologically treat POME in SBR and WAS can be potentially used as the adsorbent in the physical treatment of SBR effluent with commendable efficiency.

CHAPTER 1

INTRODUCTION

1.1 Palm oil in Malaysia

Malaysia is one of the largest producers of palm oil in the world. The production contributes around 39% of the total palm oil production in the world and 44% of world's export (MPOC, 2009). As per 2009, the cultivation of oil palm tree has reached 4.49 million hectares in Malaysia alone. This mass plantation has enabled Malaysia to produce 17.73 million tonnes of palm oil and 2.13 million tonnes of palm kernel oil (MPOC, 2009).

However, the mass production of palm oil has significantly contributed towards the environmental pollution. It is mainly caused by the abundant of waste generated while processing the fresh fruit branch (FFB). The FFB is the source for palm oil production. The FFB will undergo several processing stages before the oil could be produced from it. The processing stages are sterilization, stripping, oil extraction, clarification and oil purification (Ma, 1999). In these processes, many types of wastes are produced. Among those wastes are empty fruit brunches (EFB), potash, palm kernel, shell, fiber and liquid waste. However, these wastes (except liquid waste) can be re-used as boiler fuel and/or fertilizer. Meanwhile, the liquid waste is normally channeled into the receiving body after treatment process.

During the process of extracting oil from the FFB, water will be used extensively. Production of 1 tonne of crude palm oil needs about 5-7.5 tonnes of water and more than 50% of the water used will end up as liquid waste (Ma, 1999). This liquid waste is commonly referred to as palm oil mill effluent (POME). POME is highly polluting agent due to its high Chemical Oxygen Demand (COD) value, suspended solids, oil and grease, and other nutrients (Ahmad et al., 2003). This could contribute towards the eutrophication, disruption in the food chain and clean water scarcity if it is released into receiving body without treatment.

Generally, the available methods for POME treatment can be classified into three major categories, namely; physical-chemical treatment, biological treatment and advanced treatment. Currently, the available techniques for POME treatment are tank digestion and mechanical aeration, tank digestion and facultative ponds, decanter and facultative ponds physio-chemical and biological treatment (Andreasen, 1982). Nevertheless, at present, 85% of all POME treatments are based on the biological anaerobic digestion, followed by aerobic oxidation in ponds (Vijayaraghavan et al., 2007). However, a major drawback of these methods is the release of harmful greenhouse gases and the effluent released does not meet limit often (Ahmad et al., 2003).

In addition, the excess generation of waste activated sludge (WAS) in biological treatment plant also poses a big threat to the efficiency of the system (Liu and Tay, 2001). WAS needs to be removed from the biological system in order to maintain a food to microorganism ratio. However, due to its high disposal cost (Horan, 1990), the WAS is rarely removed from the pond. As a result, the excess amount of sludge causes failure to the biological treatment system due to insufficient food as well as limited oxygen level for the complete oxidation.

Hence, in future, the treatment system must have the ability to treat the POME efficiently in order to curb the rising environmental pollution. Though there are some breakthroughs in terms of new treatment methods such as adsorption and membrane anaerobic system (Ahmad et al., 2005; Fakhru'l-Razi and Noor, 1999), the feasibility on the economic front and applicability at large scale is rather questionable. Thus, researches have been carried out extensively in order to find a treatment system which could arrest the environmental pollution with economically feasible process. Nevertheless, till date, the expected outcomes are yet to achieve.

1.2 Problem Statement

The current treatment system of POME usually fails to meet the regulations imposed by the Department of Environment (Ahmad et al., 2003). As a result, the environment has been affected by the improperly treated POME. Apart from that, the current open-pond biological system requires large area of land to operate. In addition, the residents nearby the palm oil mill suffer from bad odor, pollution of clean water supply and infected with deadly tropical diseases such as dengue due to this open-pond system. The sociological impact on the residents has to be addressed as well before deciding on the most suitable treatment method to treat the POME. At the same time, treatment method with lower capital cost has to be figured out without compromising the effluent quality.

Thus, combination of two or more treatment methods could be a solution for such persisting problem. The disadvantage of one treatment method could be complemented by the other treatment method. Therefore, the combination of biological treatment system and the physical treatment system would be one of the possible ways to treat POME efficiently. However, the large land area required for the conventional open-pond biological treatment system remains unresolved. Hence, in order to overcome this problem, the accumulated POME could be treated using a specifically designed sequencing batch reactor (SBR). The footprint of the SBR treatment system could be reduced by 80% and the piping system required is minimal compared to the conventional biological treatment plant (de Bruin et al., 2004).

Another major drawback of the conventional biological treatment system is the poor separation between biomass and the treated effluent (Liu et al., 2003). In order to solve the presence of sludge in the effluent, a better separation between effluent and the sludge is needed. One of the possible ways to overcome this problem is by transforming activated sludge into aerobic granule. The aerobic granule possesses excellent settling ability, subsequently achieving better separation between effluent and biomass (Arrojo et al., 2004; Liu et al., 2010). In addition, the aerobic granule is able to withstand shock loadings, survive in toxic conditions and robust (Pijuan et al., 2009). Nowadays, aerobic granulation is getting more attention particularly in the wastewater treatment (Liu et al., 2010). However, till date, no investigation has been attempted on developing aerobic granule in POME.

Meanwhile, the adsorption treatment system (physical treatment) could be a good option to be combined with the SBR (biological treatment) system. Currently, the commercial adsorbents available in the market are made from coal which is a non-sustainable raw material. Hence, possibility of utilizing alternative raw material to produce adsorbent has to be addressed. In this study, the waste activated sludge (WAS) from the SBR was used as the adsorbent. Besides being sustainable, the un-controlled generation of WAS made it abundantly available at lowest possible cost.

1.3 Objectives

The primary aim of this research is to develop a combined biological and physical treatments system for POME. The specific objectives are:

1. To develop and utilize aerobic granule in POME treatment using lab scale SBR.

2. To study the feasibility of using WAS from SBR for adsorption of Methylene Blue (MB) in batch process.
3. To study the dynamic adsorption equilibrium of MB adsorption onto WAS in a continuous flow column.
4. To optimize the combined biological and physical systems to achieve the maximum treatment efficiency.

1.4 Scope of Study

There are two major parts, which involved in this study, namely; biological and physical treatments. In the biological treatment, the aerobic granule was developed in the SBR system. The system was fed with POME at a constant organic loading rate (OLR) and activated sludge from a facultative pond of the biological POME treatment plant was used as the seed sludge. It was aerated with compressed air from the bottom of the reactor. The COD, mixed liquor suspended solids (MLSS), sludge volume index (SVI) and morphology of the sludge were recorded on a pre-determined interval. Once the aerobic granule was formed in the SBR, the effect of OLR on the granule and the granule performance in treating POME were determined.

Meanwhile, for the physical treatment of POME via adsorption method, the waste activated sludge (WAS) collected from SBR was used. Prior to the treatment of POME, the WAS was quantified for its adsorption capacity, removal efficiency, adsorption mechanism and adsorption kinetics. In order to quantify the WAS, MB dye was used as the adsorbate. The WAS was evaluated in both batch and continuous flow column systems. Both of these studies give a hindsight of the ability of WAS as an adsorbent. From there, the WAS was used to treat the effluent within the SBR (biologically treated POME) in a continuous flow column. The adsorption process of treated POME was optimized based on the two variables (bed height and flow rate of treated POME into the column), using the Response Surface Methodology (RSM).

1.5 Organization of Thesis

There are 5 major chapters in this thesis. In Chapter 1 (Introduction), a brief introduction about the palm oil in Malaysia, POME generation and current POME treatment methods are given. In addition, the need for this research to be done (Problem statement), the objectives of this research, scope of this study as well as the arrangement of this thesis has been explained in this chapter.

Next, in Chapter 2 (Literature Review), the technical aspects of this research have been discussed thoroughly. The biological treatment of POME, the application of SBR in wastewater treatment, development of aerobic granule in POME and adsorption studies on POME treatment are discussed in this chapter.

Chapter 3 (Methodology) provides the information about the materials and methods used in this research. The raw material, analyzing procedure and optimization process are discussed in detail in this chapter.

Meanwhile, in Chapter 4 (Results and Discussion), the results obtained in this research are elaborately explained. Firstly, the development of aerobic granule in the POME has been explained with the help of experimental data. Next, the performance of the developed aerobic granule in treating POME has been reported in detail. Following that, the effects on the OLR on the aerobic granule and POME treatment has been discussed as well. Apart from the biological treatment, the physical treatment of POME has been reported as well. The performance of chemically activated WAS in treating MB in batch and continuous flow column studies are reported here. The optimization process in treating biologically treated POME by using WAS has been discussed in the last part of this chapter.

In Chapter 5 (Conclusion), the conclusion drawn from this study has been reported. The conclusion was made based on the discussion made in Chapter 4. These conclusions would be able to determine whether the objectives are met or not. The recommendations are also given for the future work, based on the current study. The shortages found in this research could be addressed in the upcoming works to further enhance the treatment method used in this study.

CHAPTER 2

LITERATURE REVIEW

2.1 Palm oil mill effluent (POME)

Palm oil mill effluent (POME) is one of the abundantly produced wastes from the palm oil mill. In the processing stages of palm oil, liquid waste will be produced from the sterilization unit (60%), hydrocyclone unit (4%) and clarification unit (36%) (Borja and Banks, 1994). In POME, though water is the major component (95-96%), but there are also fibers, free organic acids, traces of oil, and suspended solids in it (Ugoji, 1997). On top of that, POME is highly polluted with organic compounds. This resulted in high value of COD and BOD value. The pH value of POME is normally in the acidic region and temperature of POME at the discharge point is normally around 50°C. However, the amount of nitrogen compounds in POME can be classified as negligible.

The compilations of characteristics of POME from several previous works are given in Table 2.1. From the Table 2.1, it is exhibited that POME is a highly polluting agent due to its COD value and other constituents. The treatment of POME is mainly aimed at reducing the COD value to the allowable limit to environment. The effluent Standards (set by Department of Environment) that the palm oil producing company has to meet are listed in Table 2.2. In order to meet the regulations (or Standards), many types of treatment system have been undertaken to treat the POME. However, due to low cost and less maintenance, the biological treatment system has been widely used at industrial level (Vijayaraghavan et al., 2007).

Table 2.1 Characteristics of POME from various works

pH	Temperature	BOD (mg/L)	COD (mg/L)	Oil and grease (mg/L)	Suspended solids (mg/L)	Nitrogen Content (mg/L)	Reference
3.5-4.5	-	11000-30000	30000-70000	5000-13000	9000-25000	500-900	Borja et al., (1996)
5	-	11000	246000	-	-	-	Oswal et al., (2002)
4.7	-	25000	50000	4000	18000	750	Ahmad et al., (2003)
4.52	-	-	70900	-	25800	-	Wu et al., (2007)
4.0-4.8	75°-90°C	-	30000-50400	1300-4700	11500-22000	660-890	Bhatia et al., (2007)
3.5-4.2	80°-90°C	10000–44000	16000-100000	-	5000-54000	-	Zhang et al., (2008)
4.15-4.45	-	21500-28500	45500-65000	1077-7582	15660-23560	300-410	Wong et al., (2009)
5.6	-	-	46000	-	42800	-	Damayanti et al., (2010)

Table 2.2 Environmental Quality (Sewage and Industrial Effluents) Regulations, 1979. Maximum Effluent Parameter Limits Standards A and B (Federal Subsidiary Legislation, 2011).

Parameters	Standard A	Standard B
pH	6.0 - 9.0	5.5 - 9.0
Temperature	40 °C	40 °C
Chemical Oxygen Demand (COD)	50 mg/L	100 mg/L
Biological Oxygen Demand (BOD)	20 mg/L	50 mg/L
Oil and grease	Not detectable	10 mg/L
Suspended solids	50 mg/L	100 mg/L

2.2 Biological treatment of POME

Biological treatment has been the preferred choice for treating POME due to its low cost, high organic loading capability, simple and low energy demand (Najafpour et al., 2006). The presence of microorganisms in the biological treatment system will facilitate the oxidation of substrate (pollutants) present in the POME.

In recent years, the 85% of the POME treatment is based on the anaerobic and facultative ponding system, which is followed by another system consisting of an open tank digester coupled with extended aeration in a pond (Ma, 1999). The aerobic ponds are necessary to reduce the COD and BOD further (Poh and Chong, 2009). However, the major drawback of this ponding system is the long hydraulic retention time (HRT) (20-200 days) (Chan and Chooi, 1984). Moreover, the aeration ponds cannot be very deep, thus, large reaction volumes are obtained by increasing the surface area. This is mainly due to difficulty in oxygen penetration to the bottom of the pond, if the pond is deep. Therefore, large land area and long HRT are required for the series of aeration pond to effectively treat the POME. Besides, the degradation of POME in the ponding system releases obnoxious gases such as hydrogen sulphide and methane, which makes the surrounding environmentally polluted.

Due to these problems, the researchers came out with alternatives to treat the POME. Borja and Banks (1994) have treated the POME with upflow anaerobic sludge blanket reactor (UASB). The results from the treatment showed that the COD was removed up to 96%. Besides that, the UASB reactor has a noteworthy advantage over the ponding system as the hydraulic retention time is much shorter and the area required for the reactor is small. One of the salient features of the UASB is the formation of granular sludge (Najafpour et al., 2006). Following the success of the upflow reactor, modification was carried out on the reactor to replace the sludge blanket with filtration unit (UASB to UAF) for POME treatment (Borja and Banks, 1994). In this method, almost 90% of the COD was oxidized and it was reported that the operation of the reactor showed good stability in acidic and alkaline condition (Borja and Banks, 1994). As discussed earlier, the ponding system could not prevent the harmful gases (methane and hydrogen sulphide) from being released to the environment. However, through the UASB and/or UAF, the methane gas could be captured in the reactor itself for the use of biomass energy production. For every 1 g of COD removed anaerobically, 0.69-0.79 dm^3 of methane gas was produced in the UAF (Borja and Banks, 1994).

Despite that, the common problem associated with the UASB is the non-operational at the high organic loading rate due to the presence of suspended solids in the POME (Najafpour et al., 2006). In order to overcome this shortcoming, the integration of UASB and Upflow Fixed Film (UFF) reactor was proposed and successfully used to treat the POME (Najafpour et al., 2006). This integrated reactor is called the upflow anaerobic sludge fixed film (UASFF). The schematic diagram of the UASFF is shown in Figure 2.1. Through the integration of UASB and UFF, the solid retention would be higher and improves the solid/liquid/gas separation in the reactor. COD removal about 97% was achieved with this reactor (Najafpour et al., 2006). Nevertheless, this integrated reactor faces problem in terms of scaling-up to the industrial usage and the high cost involved for each cycle of operation.

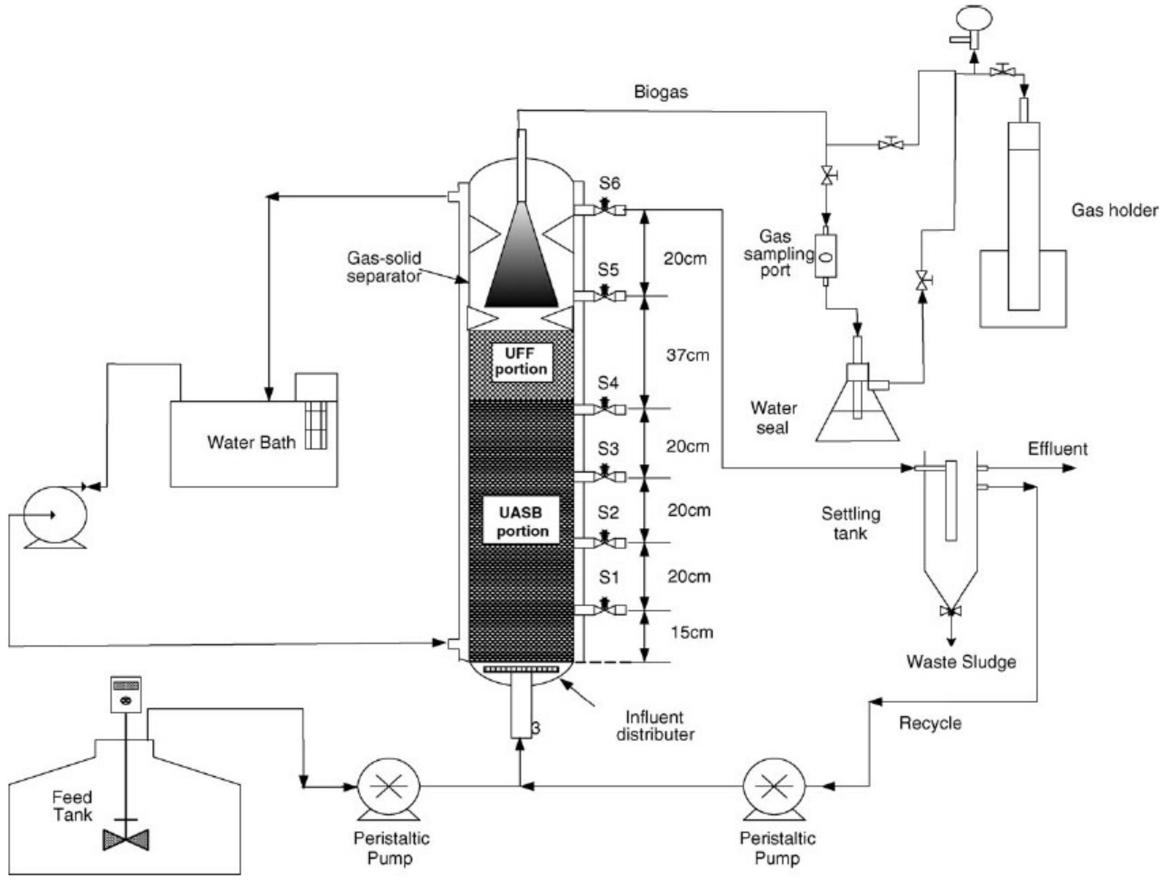

Figure 2.1 Schematic diagram of UASFF (Najafpour et al., 2006)

Meanwhile, Vijayaraghavan et al. (2007) have investigated the aerobic treatment of POME using activated sludge reactor. They reported that the COD removal achieved for aerobic treatment was 98% for HRT of 60 hours. They proved that the COD and BOD removal was higher when the HRT is extended regardless of the source of POME (Vijayaraghavan et al., 2007). The experimental set-up is shown in Figure 2.2. Besides reducing the carbon content, the use of aerobic treatment also decreases the inorganic nitrogen whilst changes the pH from acidic region into alkaline region (Agamuthu et al., 1986).

In this work, the SBR was used to treat the POME. Although SBR is frequently used to treat the industrial wastewater (Liu et al., 2004; Muda et al., 2010;

Schwarzenbeck et al., 2005) and also domestic wastewater (Ni et al., 2009) in bench and pilot plant scales, but the technology is still new to POME treatment. The SBR has many advantages over other methods and it will be further discussed in the next section.

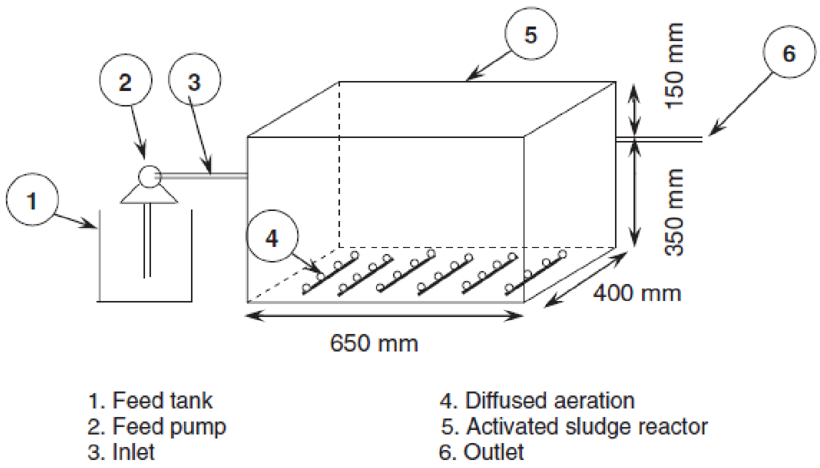

Figure 2.2 Schematic diagram of activated sludge reactor (Vijayaraghavan et al., 2007)

2.2.1 Sequencing batch reactor (SBR)

Sequencing batch reactor (SBR) is a growing technology for the treatment of wastewater in recent times. The system has been utilized to treat various sources of wastewater (Muda et al., 2010; Ni et al., 2009; Schwarzenbeck et al., 2005). It has gained interest due to its advantages in terms of land requirement, pipeworks, energy utilization and capability to be used at industrial scale (de Bruin et al., 2004). The SBR works on the time sequence basis, as the name suggests. The SBR operation consists of filling, reacting, settling, decanting and idle phases in a single cycle. This indeed reduces the space needed for various stages of treatment (de Kreuk et al., 2004), where in SBR, all could be done in one single reactor. During filling, the wastewater will be fed into the reactor. In the reaction phase, the microorganism will oxidize the organic content of the wastewater fed into it with the aid of aeration supplied. Next, in the settling phase, the sludge is allowed to settle for the separation of sludge and the supernatant. In the decanting phase, certain volume of the supernatant will be decanted from the reactor. The last phase of a cycle is the idle phase. In this phase, the reactor will be left rest before proceeding to the next cycle. A typical SBR operation is shown in Figure 2.3.

Among the industrial wastewater treated in SBR was POME. However, this treatment was carried out using a lab-scale system (Chan et al., 2010). The BOD and COD removal achieved were in the ranges of 91-96% and 92-99%, respectively. Besides high COD and BOD removal, the SBR operates with short HRT. In the POME treated using SBR, the maximum HRT was 3 days instead of 40 days in anaerobic digestion system (Chan et al., 2010; Fun et al., 2007). Besides that, bad odor from the anaerobic digestion system could be prevented by the aerobic treatment in SBR.

Though the POME has been successfully treated in the SBR, there are some problems which are yet to be resolved. The floccular sludge used in the SBR treatment of POME resulted in a very poor settling ability. Hence, longer time is needed for the settling of the biomass and yet the effluent would not be completely free of unsettled biomass. This problem could only be solved by using an aerobic granular sludge.

In SBR, granulation technology could be easily developed and operated. The granule has settling ability and can offer good solid-liquid separation (Jang et al., 2003). The granulation is possible in this reactor due to the height over diameter

(H/D) ratio which reported to provide better selection pressure for settling granule (Kong et al., 2009). In the granulation technology, two major kinds of granulations are available, namely anaerobic and aerobic. The aerobic granulation technology utilized at industrial level is still scarce. Moreover, the aerobic granulation technology is yet to be applied in POME treatment.

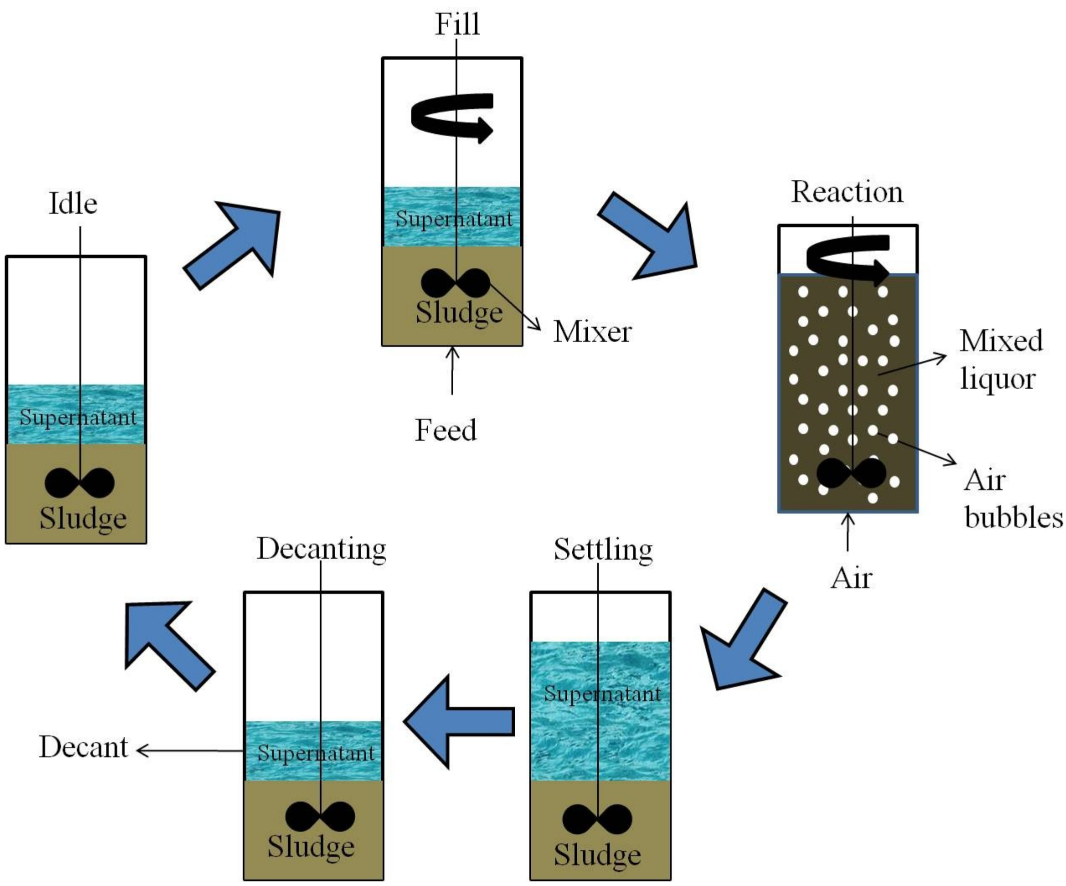

Figure 2.3 SBR operation (adapted from (Metcalf and Eddy, 2003))

2.2.2 Aerobic granule

Aerobic granule is the aggregation of microorganism into compact and spherical shape with clear boundaries under the influence of air (Liu et al., 2010). The aerobic granule have been successfully developed and used in the treatment of wastewater in the SBR by several researchers (Li et al., 2010; Muda et al., 2010; Ni et al., 2009;

Song et al., 2009). Some of the granule were developed using synthetic wastewater such as glucose, sodium acetate, phenol and tert-butyl alcohol are shown in Figure 2.4. According to Liu et al., (2010) the cultivation in various sources of wastewater proves that the aerobic granulation is independent of the substrate.

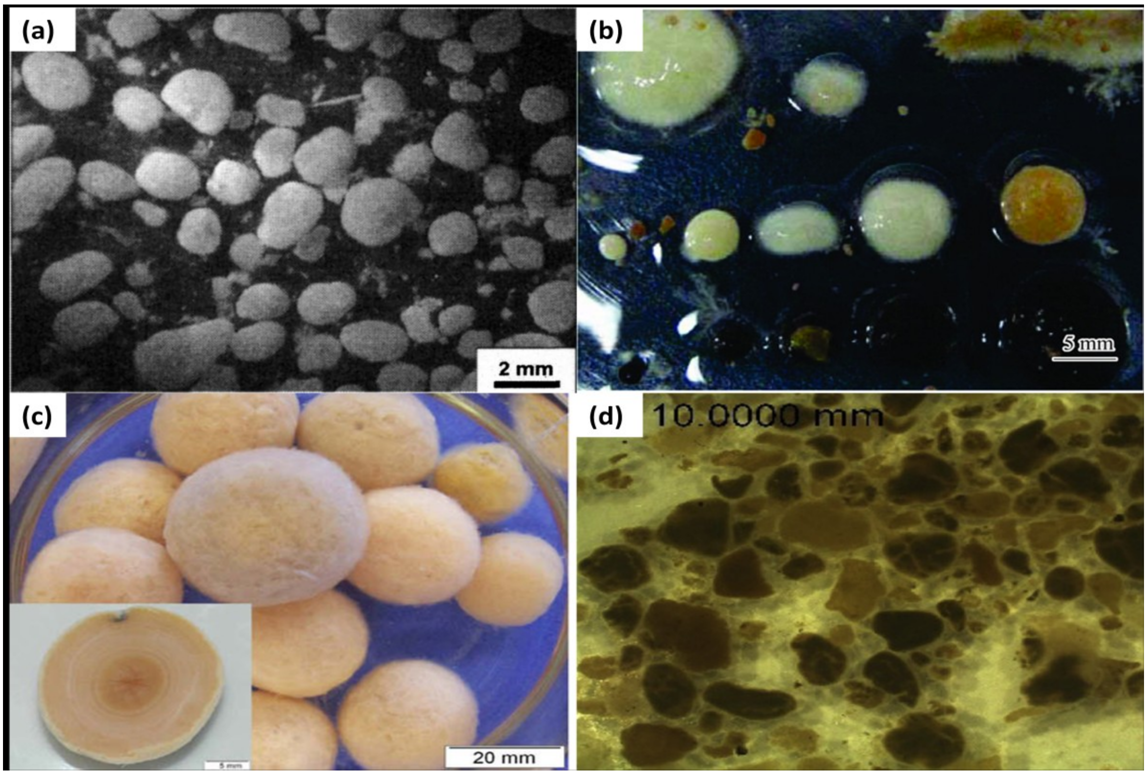

Figure 2.4 Aerobic granule developed by (a) (Tay et al., 2004) (b) (Li et al., 2010) (c) (Li et al., 2010) and (d) (Muda et al., 2010)

Aerobic granule has many advantages such as excellent settling ability with minimum biomass in the effluent (Arrojo et al., 2004; Liu et al., 2010). Besides, aerobic granule are also robust, stable and capable to withstand any shock loading of organic content (Adav et al., 2008; Tay et al., 2002) and maintain their characteristics even after long starvation periods which can occur due to seasonal closure of the industries (Pijuan et al., 2009). Aerobic granulation forms due to the aggregation of self-immobilized microorganisms present in the reactor (Shi et al., 2010) and has been shown to be influenced by several factors such as hydrodynamic shear force, settling time, feeding strategy and dissolved oxygen (Kong et al., 2009). Once it has formed, the aerobic granule would not remain at the same size. The rate of detachment and attachment of biomass on the aerobic granule determines the size of them (Liu and Tay, 2002).

The hydrodynamic shear force has a major contribution in the formation of aerobic granule. The flow rate of the supplied air is manipulated to provide a desired hydrodynamic shear force. An increase in hydrodynamic shear force will enhance the production of extracellular polymeric substances (EPS) (Tay et al., 2001). The EPS functions to aggregate the microorganism in a cluster and subsequently forming aerobic granule. The secretion of EPS by the microorganism at a high aeration rate also facilitates the increase in diameter of the aerobic granule.

Meanwhile, the settling time also plays a crucial role in the formation of aerobic granule. In order to promote granulation, the settling time has to be low. Adav et al. (2009) investigated the settling time effects by working at the three different settling times (10, 7 and 5 minutes) and reported that the species of microbial community present in the reactor changes with settling times. A low settling time will allow only the denser particle to remain in the reactor, while the lighter and poor settling biomass will be removed from the reactor (Liu and Tay, 2004). The desired morphology of aerobic granule is free of filamentous growth around the edges. The aerobic granule with filamentous growth generally has a poor settling ability. The low settling time will remove the filamentous aerobic granule and enhance the population of compact aerobic granule in the reactor. Such a low settling time also contributes to faster appearance of aerobic granule (Adav et al., 2009). Furthermore, the low settling time was also found to enhance the EPS secretion and cell hydrophobicity (Liu and Tay, 2004).

Cell hydrophobicity is another important factor in the formation of aerobic granule. Hydrophobicity of the biomass will assist the aggregation process (Tay et al., 2001) and subsequently leads to aerobic granulation. Cell hydrophobicity would mainly occur when there is a starvation period within an operational cycle of SBR. Once the substrate in the SBR has been consumed, the biomass will be under starvation. It was reported that the aggregation of the biomass is one of the techniques to overcome the effect of starvation (Liu and Tay, 2004).

Meanwhile, organic loading rate (OLR) has an impact on the size of the aerobic granule. Generally, for aerobic granulation purpose, a wide range of OLR (2.5 to 15 kg COD/m^3.day) was used (Liu et al., 2003). The work undertaken by Adav et al. (2009) reveals that when the OLR was increased, the mean diameter of the aerobic granule increased from 2.7 to 5.1 mm. Nevertheless, an increase of OLR does not affect the COD removal. The work carried out by Thanh, (2005) exhibited the efficiency of the developed aerobic granule in various OLR which remained close to 100% even when the OLR was increased gradually. This further proves that the aerobic granule is feasible to be used in the highly fluctuating wastewater quality.

2.3 Physical treatment of POME

The previous studies have proven that POME can be treated by physical treatment as well. Physical treatment is inclusive of coagulation-flocculation, membrane treatment and adsorption. Physical treatment is easier to be handled compared to the biological treatment (Bhatia et al., 2007). However, the cost of operating physical treatment is relatively high compared to biological treatment plant. Several researchers have studied on POME treatment using adsorption method (Ahmad et al., 2005), membrane technology (Ahmad et al., 2006) and coagulation-flocculation (Bhatia et al., 2007).

Various levels of treatment efficiencies have been achieved by using those physical treatment methods. The most effective treatment system was the membrane system. Almost 99% of the COD has been removed from the influent (Ahmad et al., 2003). Despite the excellent performance of the membrane system, the cost of operating at industrial level and the membrane fouling has prevented it to be up-scaled into industrial level. However, the work on adsorption process to remove COD and turbidity has not been fully explored till date. In this work, the feasibility of adsorption system was studied, which aim is to remove COD and turbidity of the biologically treated POME.

2.3.1 Adsorption

Adsorption process is mainly used in water/wastewater treatment system, trapping volatile organic component (VOC) and removing heavy metal ions. According to Slejko, (1985), adsorption is a process of separating a substance from a solution with the accumulation of the solute on the surface of other materials. The adsorbing agent is termed as adsorbent, while the material concentrated at the surface of that agent is termed adsorbate. There are two main types of adsorption process. They are chemical adsorption (chemisorption) and physical adsorption (physisorption) (Slejko, 1985). The adsorbent has pores on its surface. During an adsorption process, adsorbate will accumulate on the surface of the pores of the adsorbent. This process will continue until the adsorbent becomes saturated. Once it becomes saturated, the rate of adsorption and desorption will reach an equilibrium state which can be regenerated by using heat. The adsorption mechanism is shown in the Figure 2.5.

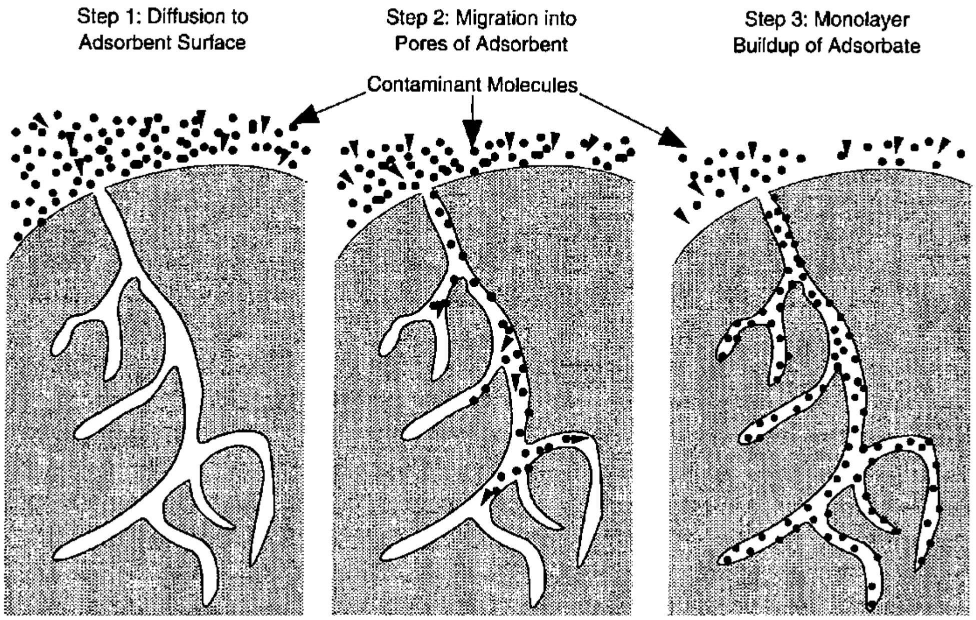

Figure 2.5 Adsorption mechanism (Wu, 2008)

According to Slejko (1985), the physical adsorption process is a result from the action of van der Waals forces which consist of electrostatic forces and London dispersion forces. It exhibits a weak bonding between the liquid and solid (adsorbent) in the liquid-solid adsorption process. The force of attraction between the adsorbate and substrate is contributed by the instantaneous fluctuating electric dipole moments. These dipole-dipole forces are called the 'van der Waals' forces.

Besides that, physical adsorption is an exothermic process. It releases approximately 0.1 kcal/mole of energy at each time reaction taking place (Wu, 2008). Physisorption process is a reversible process. Hence, it is easy to regenerate the adsorbent used as it is aided by the properties of physisorption. The chemical identity of the adsorbate remains intact as there is no breakage of covalent bonding of the adsorbate. In physisorption, the layers of absorbate that can be formed on the adsorbent could be multilayer or single layer. Stoltenberg et al., (2005) reported that the binding energy of the physisorption is between 50-500 meV per atom or molecule. The operating range of temperature for the physisorption process is normally near or below temperature at which the adsorbate will condense from gas to liquid phase.

Meanwhile, chemical adsorption is based on chemical bond between the adsorbent and the substrate. The strength of this reaction is stronger than the physisorption. Drago et al., (1998) reported that dissociation of the adsorbate after the adsorption process occasionally happens due to the chemisorption which can be stronger than the internal bonds of the free adsorbate. Generally, the chemisorption process is endothermic in nature. Moreover, the chemisorption process is an irreversible process. Hence, the regeneration of the adsorbent is quite impossible. In addition, the chemisorption only forms a single layer of adsorbate on the adsorbent in comparison to the physisorption. The chemisorption can usually occur over a wide range of temperature and not limited as that of the physisorption.

2.3.2 Adsorbent

Currently, activated carbon is used as adsorbent in wastewater treatment (Thinakaran et al., 2008; Wu and Tseng, 2008). The high operating and regeneration costs of the process, as well as the high price of activated carbon, make it unsuitable for large scale operation (Crini, 2006). Hence, the researchers began to switch the starting material (raw material) to alternatives available for them.

The agro based activated carbon garnered attention due to reliability in getting the raw material. Bamboo has been used as the adsorbent to remove MB via adsorption (Hameed et al., 2007). The maximum monolayer adsorption capacity documented was 454.2 mg/g. Coconut shell also has been utilized as the adsorbent in removing Basic Green 4 dye (Nuithitikul et al., 2010). The maximum monolayer adsorption capacity recorded was 322.6 mg/g. The adsorption process is not just limited to synthetic dye removal. It has been reported that the COD of a wastewater can be reduced by adsorption. Date pit (more than 80% removal), rice husk (around 70% removal) and avocado peel (about 99.18% removal) have been successfully used to remove the COD from the wastewater (Devi et al., 2008; El-Naas et al., 2010; Mohan et al., 2008).

In addition to the agro based activated carbon, waste products such as waste activated sludge (WAS) also has shown capability to be an adsorbent. Various pollutants, such as metal ions, synthetic dye and organic compounds have been removed from the wastewater (Luo et al., 2006; Tsai et al., 2008; Wang et al., 2008). The already existing functional groups on the surface of the WAS have aided the adsorption process.

2.3.3 Waste activated sludge

Despite many advantages of biological treatment system (as explained in section 2.1), one of the major drawbacks of the system is the continuous generation of WAS. The excess production of WAS from biological wastewater treatment (BWT) plants poses a serious problem because the handling and disposal of it often represents the largest operational cost (Horan, 1990). Usually, removed WAS was disposed off in landfills or occasionally used as fertilizer (Otero et al., 2003).

Hence, researchers have explored the potential of WAS as a color adsorbent in the attempt to increase its economical value (Caner et al., 2009; Ju et al., 2008; Smith et al., 2009; Sun et al., 2008). The presence of various functional groups in the

WAS aids the color adsorption (Aksu, 2001). The functional groups that exist on WAS include -OH, -NH, $-NH_2$, -C=O, C=C, CH_3-, and CH_2- (Luo et al., 2006). Previous researchers mainly studied the WAS produced from municipal sewage treatment plants to remove Rhodamine-B (Ju et al., 2008), Burazol Blue ED (Caner et al., 2009) and Malachite Green (Sun et al., 2008).

In this work, the WAS from POME treatment plant was used to remove the COD and turbidity of POME.

2.3.4 Batch equilibrium isotherm

Generally, the equilibrium isotherm is used to show the interaction between adsorbate and adsorbent in equilibrium phase (El Qada et al., 2006). Marina et al., (2007) suggested that among the common models used are the Langmuir and Freundlich as these models are relatively simple and widely used. The validity of the isotherm models are chosen based on the correlation coefficients (R^2).

2.3.4 a) Langmuir isotherm model

Langmuir isotherm was developed with three major assumptions (Slejko, 1985). The assumptions are i) Adsorption energy is constant and independent of surface coverage, ii) Adsorption occurs at localized sites with no interaction between adsorbate molecules, iii) Maximum adsorption occurs when the surface is covered by a monolayer of adsorbate. The Langmuir equation is represented by equation (2.1).

$$q_e = \frac{Q_o K_c C_e}{1 + K_c C_e} \tag{2.1}$$

where, q_e is the amount of adsorbate uptake at equilibrium (mg/g), Q_o is the maximum monolayer adsorption capacity (mg/g), K_c is equilibrium constant (l/mg), and C_e is the equilibrium concentration of adsorbate (mg/l).

This equilibrium isotherm has been used by many researchers. Hameed et al., (2007) fitted the Langmuir isotherm for MB adsorption process onto bamboo based activated carbon. In addition, Weng et al., (2009) have used the Langmuir isotherm model to determine the distribution of MB on pineapple leaf powder at equilibrium state.

2.3.4 b) Freundlich isotherm

Freundlich isotherm assumes that the adsorption occurs on a heterogeneous energy surface and the adsorption capacity depends on the MB concentration at equilibrium (Caner et al., 2009). The Freundlich equation is given in equation (2.2).

$$q_e = K_f C_e^{1/n} \tag{2.2}$$

where, q_e is the amount of adsorbate uptake at equilibrium (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/l), K_f and n are the Freundlich constants.

Vadivelan and Kumar, (2005) have applied the Freundlich isotherm in the adsorption of MB onto rice husk and found this isotherm fitted their data well. Besides, Nasuha and Hameed, (2011) also utilized this model for the adsorption of MB onto rejected tea and R^2 value was found to be 0.934, which is highly acceptable.

2.3.5 Batch adsorption kinetic models

Adsorption occurs by a multistep mechanism comprising: (i) diffusion across the liquid film surrounding the solid particles (external mass transfer coefficient as limitation), (ii) diffusion within the particle itself assuming a pore diffusion mechanism (intraparticle diffusion) and (iii) physical or chemical adsorption at a site (Kumar et al., 2005). Hence, in order to identify the rate-limiting step, the kinetic models were fitted to the data. There are two common adsorption kinetic models used frequently. One is being pseudo-first order model, while the other is pseudo-second order model.

2.3.5 a) Pseudo-first order model

This model was first proposed by Lagergren with the equation (2.3).

$$\ln(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (2.3)$$

Where, k_1 is the rate constant (1/min), q_e is the amount of solute adsorbed on the surface at equilibrium (mg/g), q_t is the amount of solute adsorbed at any time (mg/g) and t is the time (s).

Arzu and Kalayci, (2005) have used this kinetic model in the adsorption of phenol onto chitin. In addition, Hameed et al., (2009) also modeled the adsorption of MB onto pineapple waste by using this kinetic model.

2.3.5 b) Pseudo-second order model

The pseudo first order kinetics has limitation as it cannot fit well for whole range of contact time. According to Ho and McKay, (1999), it is applicable only for the initial stage of adsorption process. Hence, Ho and McKay, (1999) proposed a pseudo-